

# COMBUSTION OF ORGANIC MOLECULES BY THE THERMAL DECOMPOSITION OF PERCHLORATE SALTS: IMPLICATIONS FOR ORGANICS AT THE MARS PHOENIX SCOUT LANDING SITE.

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**Introduction:** The Mars 2007 Phoenix Scout Mission successfully landed on May 25, 2008 and operated on the northern plains of Mars for 150 sols. The primary mission objective was to study the history of water and evaluate the potential for past and present habitability in Martian arctic ice-rich soil [1]. Phoenix landed near 68° N latitude on polygonal terrain created by ice layers that are a few centimeters under loose soil materials. The Phoenix Mission is assessing the potential for habitability by searching for organic molecules in the ice or icy soils at the landing site. Organic molecules are necessary building blocks for life, although their presence in the ice or soil does not indicate life itself. Phoenix searched for organic molecules by heating soil/ice samples in the Thermal and Evolved-Gas Analyzer (TEGA, [2]). TEGA consists of 8 differential scanning calorimeter (DSC) ovens integrated with a magnetic-sector mass spectrometer with a mass range of 2-140 daltons [2]. Endothermic and exothermic reactions are recorded by the TEGA DSC as samples are heated from ambient to ~1000°C. Evolved gases, including any organic molecules and their fragments, are simultaneously measured by the mass spectrometer during heating.

Phoenix TEGA data are still under analysis; however, no organic fragments have been identified to date in the evolved gas analysis (EGA). The MECA Wet Chemistry Lab (WCL) discovered a perchlorate salt in the Phoenix soils and a mass 32 peak evolved between 325 and 625°C for one surface sample dubbed “Baby Bear” [3]. The mass 32 peak is attributed to evolved O<sub>2</sub> generated during the thermal decomposition of the perchlorate salt. Perchlorates are very strong oxidizers when heated, so it is possible that organic fragments evolved in the temperature range of 300-600°C were combusted by the O<sub>2</sub> released during the thermal decomposition of the perchlorate salt. The byproduct of the combustion of organic molecules is CO<sub>2</sub>. There is a prominent release of CO<sub>2</sub> between 200-600°C for several of the Phoenix soils analyzed by TEGA. This low temperature release of CO<sub>2</sub> might be any combination of 1) desorption of adsorbed CO<sub>2</sub>, 2) thermal decomposition of Fe- and Mg-carbonates, and 3) combustion of organic molecules [2].

The objective of this paper was to conduct laboratory experiments in a thermal and evolved gas analysis

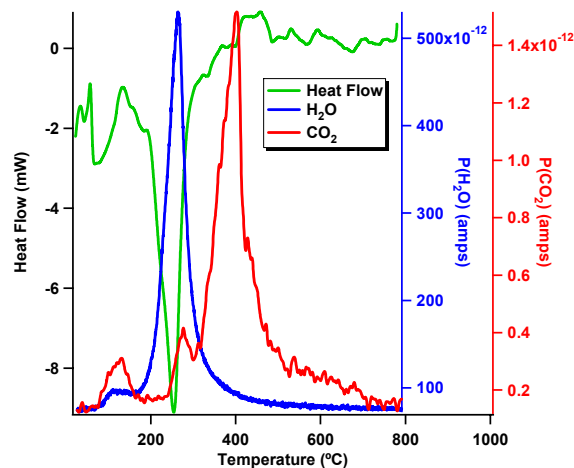
testbed to understand the effects of the thermal decomposition of perchlorate salts on organic molecules.

**Materials and Methods:** A three component mixture was designed to simulate the thermal decomposition of perchlorate salt in the presence of organic material. The mixture consisted of 2.3 wt. % Mg-perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O), 8.4 wt. % mellitic acid, and 87.3 wt. % SiO<sub>2</sub>. Mg-perchlorate was chosen because it is a leading candidate for the perchlorate salt in the Phoenix soils [3]. Mellitic acid (benzenhexacarboxylic acid, C<sub>6</sub>(CO<sub>2</sub>H)<sub>6</sub>) was chosen as the test organic material because it has been suggested to be a metastable decay product from the oxidation of kero-gens that have “rained down” on the Martian surface from meteoritic infall [4,5]. The SiO<sub>2</sub> is inorganic, non-reactive filler that has been heated in the presence of O<sub>2</sub> to 1000°C to combust any organic contaminants. The relative amounts of Mg-perchlorate and mellitic acid are arbitrary and additional runs are being conducted varying the relative proportions of the three components.

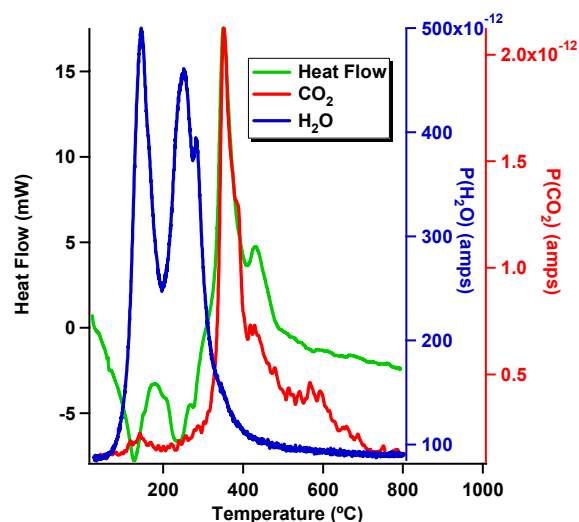
The thermal and evolved gas testbed consisted of a Setaram SENSYS Evolution differential scanning calorimeter (DSC) integrated with a Pfeiffer quadrupole mass spectrometer. The DSC has a temperature range from ambient to 830°C. Operating conditions for the DSC were 1000 mb oven pressure, ultrapure N<sub>2</sub> carrier gas, 20 sccm gas flow rate, and 20°C/min temperature ramp rate.

**Results:** Mellitic acid begins to decompose at 190°C. Water begins to evolve at 190°C and corresponds to the onset temperature for a very pronounced endothermic reaction (Fig. 1). The water release results from dehydroxylation. The next major event begins at 300°C where a large amount of CO<sub>2</sub> is driven off. Mellitic acid begins to “melt” at 300°C. No organic fragments were observed during the release of CO<sub>2</sub>; however, experiments are now underway to closely look for evidence of organic fragments in the evolved gases.

Mg-perchlorate has three water releases with onset temperatures at 85°C, 155°C, and 195°C [6]. A major exothermic reaction begins at 435°C, which is due to the breakdown of perchlorate with the evolution of O<sub>2</sub> and Cl gaseous species and the subsequent formation of MgO [6].



**Figure 1.** Thermal and evolved gas analysis for mellitic acid. A major endothermic peak with an onset temperature of 190°C is in response to dehydroxylation of structural hydroxyls. Carbon dioxide evolution has an onset temperature of 300°C.



**Figure 2.** Thermal and evolved gas analysis for mellitic acid and Mg-perchlorate mixture. Two low temperature endothermic peaks with onsets near 85°C and 190°C correspond to dehydration of water in Mg-perchlorate and dehydroxylation of structural OH in mellitic acid (see text). A major exothermic peak with an onset temperature near 300°C corresponds to the combustion of mellitic acid and the subsequent release of CO<sub>2</sub>. The second exothermic peak with an onset around 435°C is due to the thermal decomposition of Mg-perchlorate to MgO.

Two water releases (onsets at 85 and 190°C) are apparent in the mixture of Mg-perchlorate and mellitic acid (Fig. 2). The lower temperature water release results from the dehydration of Mg-perchlorate and the higher temperature release is caused by a combination of dehydration of Mg-perchlorate and the dehydroxylation of mellitic acid. A very strong exothermic reaction with an onset near 300°C is accompanied by CO<sub>2</sub> evolution. This exothermic reaction is not present in thermal analysis for samples containing only mellitic acid or only Mg-perchlorate [6]. This strong exothermic reaction is attributed to the combustion of mellitic acid. The combustion is prompted by the release of O<sub>2</sub> from the thermal decomposition of the Mg-perchlorate. The evolution of O<sub>2</sub> occurs at a higher temperature in experiments where only Mg-perchlorate is present. The mechanism for the evolution of O<sub>2</sub> at a lower temperature in the mellitic acid and Mg-perchlorate mixture is not understood and additional experiments are currently underway to resolve this issue. No organic fragments were detected in the evolved gas analysis of the mellitic acid and Mg-perchlorate mixture.

**Implications for Mars.** The presence of a strong oxidizer (i.e., perchlorate salt) in the soils at the Phoenix landing site will most likely combust organic materials during pyrolysis by TEGA. Therefore, it is highly likely that no organic fragments will be detected by TEGA, unless they are present at concentrations that can overwhelm the oxidant. No organic fragments have been detected by TEGA; although mass spectra are still being calibrated and analyzed by the Phoenix science team for possible organic fragments. We are currently examining the thermal analysis results for Phoenix soils, searching for exothermic peaks in the 300 to 500°C region.

Viking GC/MS instruments did not detect organic molecules down to the parts per billion level [7]. Organics (if they exist) at the Viking sites may have been combusted by the thermal decomposition of perchlorate salts if perchlorate salts are more widespread in soils than just at the Phoenix landing site.

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**References.** [1] Smith, P., et al., (2008), *JGR*, doi:10.1029/2008JE003083. [2] Boynton, W.V., et al., (2009, submitted), *Science*. [3] Hecht, M.H., et al., (2009, submitted), *Science*. [4] Brenner, S.A., et al., (2000), *PNAS*, 97:2425-2430. [5] Archer, P.D., et al., (2009), *LPSC XL*, this volume. [6] Lauer, H.V., Jr., et al., (2009), *LPSC XL*, this volume. [7] Biemann, K., et al. (1977), *JGR*, 30:4641-4648.